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COMPOSITION OF TRACE MINERAL INCLUSIONS IN CASSITERITE, FROM POINT X-RAY SPECTRAL ANALYSIS

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ABSTRACT: X-ray microanalysis of black cassiterite from the Etyka tin deposit of Transbaykalia revealed the presence of trace amounts of, Nb, Ta, Fe, Mn, W, Ti, Zr, Sc, Al, Si, As, Ga, V, Be, Pb, Cu, Ca, Mg and In.

Distinctive features of the chemical composition of cassiterite have long been attracting the attention of the investigators, because they constitute the basis of /214* the typical properties of this mineral and afford a fair degree of certainty in determining the origin of tin ore deposits, and consequently the practical value of the latter.

As we know, this subject has been discussed in the Soviet Union by A. M. Boldyreva (1941), Ya. D. Gotman (1941), G. L. Vazbutskiy (1941), I. F. Grigor'ye (1945), M. I. Itsikson and A. K. Rusanov (1946), I. F. Grigor'yev and Ye. I. Dolomanova (1951), Ye. I. Dolomanova (1959), G. B. Zhilinskiy (1955), and others.

As a result of the study of cassiterite from various formations and ore deposits by these investigators, the following trace minerals have been identified as additions in its crystals: tapiolite, wolframite, rutile, arsenopyrite, pyrite, zircon, quartz, light-colored mica (muscovite and zinnowaldite), and -- less certainly -- hematite and magnetite.

The dimensions of these mineral inclusions are variable, but only those grains visible under the conventional light microscope can be positively identified.

In most instances the crystals of colored trace minerals are so fine as to be translucent, appearing drab-colored, red, brown, and yellow. Similar coloring has been observed in many cassiterite zones free of any minerals visible under the microscope. A belief has arisen in this connection that these colored zones contain the same minerals but in considerably smaller particles. This /215 has been indirectly corroborated by the composition of the colored zones (as determined by spectral analysis) similar to that of zones containing the additive mineral inclusions. Some cassiterite zones contain several minerals. Such zones are colored differently from segment to segment. Depending on the quantity of the additives, the zones take on different hues of the above-mentioned colors. In some instances the color are "superimposed" over each other.

As a rule, the added trace-minerals are regularly distributed within the growth zones of the cassiterite crystals (Grigor'yev and Dolomanova, 1951; Dolomanova, 1959).

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*Numbers in the margin indicate pagination in the foreign text.

Because of the small size of added mineral inclusions, many of them remained unidentified in diagnosis by the conventional methods. The recently developed point x-ray spectral microanalysis makes possible a more complete and accurate analysis of the composition of trace minerals -- even when their grains measure 1-2 microns.

We have selected for that purpose first generation black cassiterite from the Etyka deposit, Transbaykalia; it is the richest in the additive minerals.

The Etyka tin ore deposit belongs to the cassiterite-feldspar-quartz formation, by its genetic features (Grigor'yev and Dolomanova, 1956). The ore-bearing veins occur in Lower Jurassic areno-argillaceous rocks. The veins are made up of quartz, amazonite, topaz, zinnwaldite and cassiterite; albite, fluorite, wolframite, smirnowskite, arsenopyrite, pyrite, stannite, sphalerite, chalcopirite and galena are less abundant; pyrrhotite, rutile, apatite, magnetite, triplite, chlorite, sericite, etc. are rare.

Cassiterite is crystallized in vein walls, along with topaz and quartz, locally in radial aggregates of a mixed cassiterite-topaz composition. Some of these elongated cassiterite bodies send off branches that cut the topaz. Cassiterite seldom forms inclusions in topaz; more often, it fills interstices among the topaz grains, along with zinnwaldite and first generation quartz. Locally, topaz, too, fills space among the cassiterite crystals. In quartz, cassiterite is more common in inclusions corroded by the quartz and amazonite. Cassiterite does occur with smirnowskite, although their age relationship is obscure: cassiterite inclusions in smirnowskite and the latter's corrosion by cassiterite are rarely observed. Zinnwaldite, pyrite, fluorite, second generation cassiterite, and other minerals penetrate the cracks in cassiterite. Cassiterite is corroded by the sulfides.

Cassiterite aggregates are unevenly distributed in the vein: either forming a continuous fringe along the walls or else occurring in isolated bodies alternating with topaz, zinnwaldite, and quartz. Their dimensions are small -- 1-2 cm across, often less. There are rare isolated small crystals (2-3μ long) with a simple exterior form: a combination of tetragonal prism and pyramid, at times joined in polysynthetic twins. Even finer bipyramidal cassiterite crystals are characteristic of topaz greisens adjacent to the veins.

Cassiterite is represented by three generations, with the first generation /216
cassiterite predominant in the veins. It is black in color, brittle, with a metallic to dull luster.

Other characteristic features of Etyka cassiterite are its zonated structure and marked fluctuations in the content of additive trace minerals in the individual zones. They dominate over cassiterite in some zones, are very scarce in others, and about 50-50 with cassiterite in still others (Fig. 1). Zones saturated with the additive minerals often are repeated within the cassiterite aggregate; however, there is no pattern in their recurrence.

Depending on the disposition and combination of the additive minerals, the zones are either darker or lighter. Those zones with larger ore mineral inclusions show black in addition to other colors. Such zones are non-transparent and black when their content of additive minerals is high. Cassiterite is

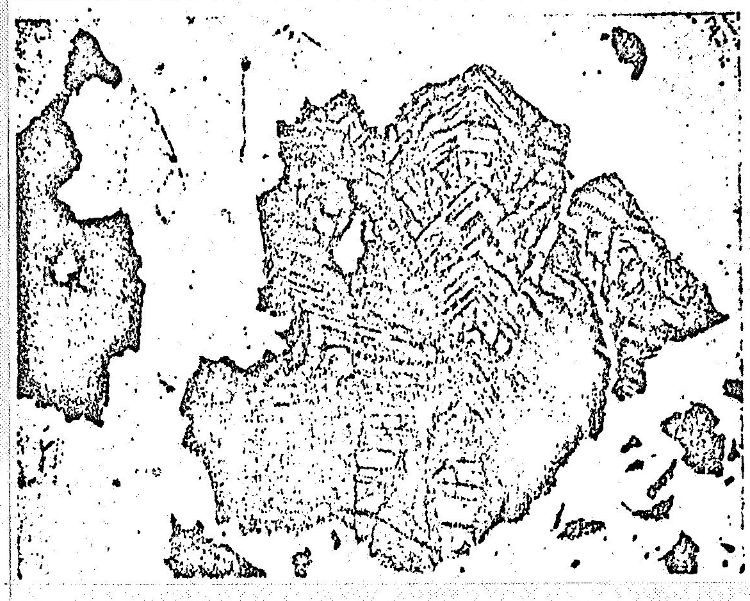

Figure 1. Zonated Cassiterite From the Etyka Ore Deposit.
(Thin Section, Single Nicols. Magnif. x 10)

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transparent -- red, brown, and other colors -- in segments with a low content of the impurities.

Cassiterite segments with a high content of ore minerals take better polish and have a higher reflection capacity as compared with the "purer" ones, free of the added minerals.

The high content of various additive minerals in cassiterite renders it very brittle and porous -- because of the rather loose bond among the various trace-minerals and between them and cassiterite. Accordingly, specific weight of black cassiterite is less than for the light-colored.

The following have been identified in cassiterite by the qualitative spectral analysis: Nb, Ta, Fe, Mn, W, Ti, Zr, Sc, Al, Si, As, Ga, V, Be, Pb, Cu, Ca, Mg and In.

The chemical analysis of black cassiterite is as follows (in %): SnO_2, 93.52; /219
SiO_2, 0.92; TiO_2, 0.87; ZrO_2, 0.54; WO_3, 0.60; Fe_2O_3, 0.38; $(Ni, Ta)_2O_5$, 1.04; MnO, 0.84; Al_2O_3, 1.07; CaO, 0.06; MgO, 0.02; total, 99.86; specific weight, 6.547. (M.O. Steppan, Analyst.)

The qualitative x-ray -- chemical analysis of black cassiterite is as follows (in %): Zr, 0.2; W, 3.0; Nb, 1.0; Ta, 0.6. (I.B. Borovskiy, Analyst.)

The microanalysis not only corroborated the presence of some of the above-named trace minerals in cassiterite, such as wolframite and rutile, but identified new ones, whose presence had been unknown or unsubstantiated: for instance hematite (Figs. 2-c and 4-c), ilmenite with added niobium (Figs. 3-a-b-c-d-e), and rutile (Figs. 3-e and 4-d). In addition, close growths of some minerals have been observed, as witness the lack of picture coincidence in the $Fe_{K\alpha}$ and $Ti_{K\alpha}$ radiations (Fig. 2) and the result of quantitative analysis at point A (Fig. 2) where the content of Fe is 52.5% and of Ti -- 19.4% (without a correction for fluorescent radiation).

Assuming that these elements are components of the oxides (as long as no other elements were observed at that point), we obtain TiO_2, 32.4% and Fe_2O_3, 68.9% (total, 101.3%).

It is possible that more than one mineral are grown together at this point.

Such joint growths of tapiolite and wolframite in the very same cassiterite have been observed under the light microscope. Obviously, such joint growth of different minerals, and their inclusions in other minerals are common in nature. For instance, P. Ramdor (1962, p. 952) notes that hematite from the Pululus tin ore deposit, Argentine, contains minute bodies (less than 1μ), evidently of cassiterite, showing the form common in rutile.

The presence of wolframite was demonstrated in scanning an inclusion of this mineral with an electron ray (Fig. 6). The wolframite contains considerably more iron than manganese. Of particular interest is the finding of corundum inclusions in cassiterite; in electron radiation, these luminesce scarlet, typical of ruby (Fig. 7-a-c-d). The presence of this mineral is corroborated also by the x-ray spectrogram (Fig. 8). /221

Just as interesting is another mineral consisting of copper and chlore (Fig. 7-a-e-f). By determining its copper content, it will be possible to determine which copper chloride is present in cassiterite.

In conclusion, it should be noted that the content of additives in first generation black cassiterite from the Etyka ore deposit reaches 6.5%.

Most if not all elements identified in cassiterite enter the composition of trace minerals -- wolframite, tapiolite, rutile, ilmenite, ruby, corundum, hematite, quartz, zinnwaldite and zircon. It remains to be seen what mineral is formed by the copper chloride.

Copper chloride preserved in the cassiterite indicates that chlorine, too, participated in mineralization; however, its role remains obscure because of the high solubility of chlorides. They are preserved only under special conditions: as trace minerals in gas-liquid inclusions and, as has been determined, as trace minerals in the zones of cassiterite growth. Further study of the composition of cassiterite and other elements evidently will identify another series of unusual trace minerals. Such investigations are quite important in understanding the mineralization processes in nature.

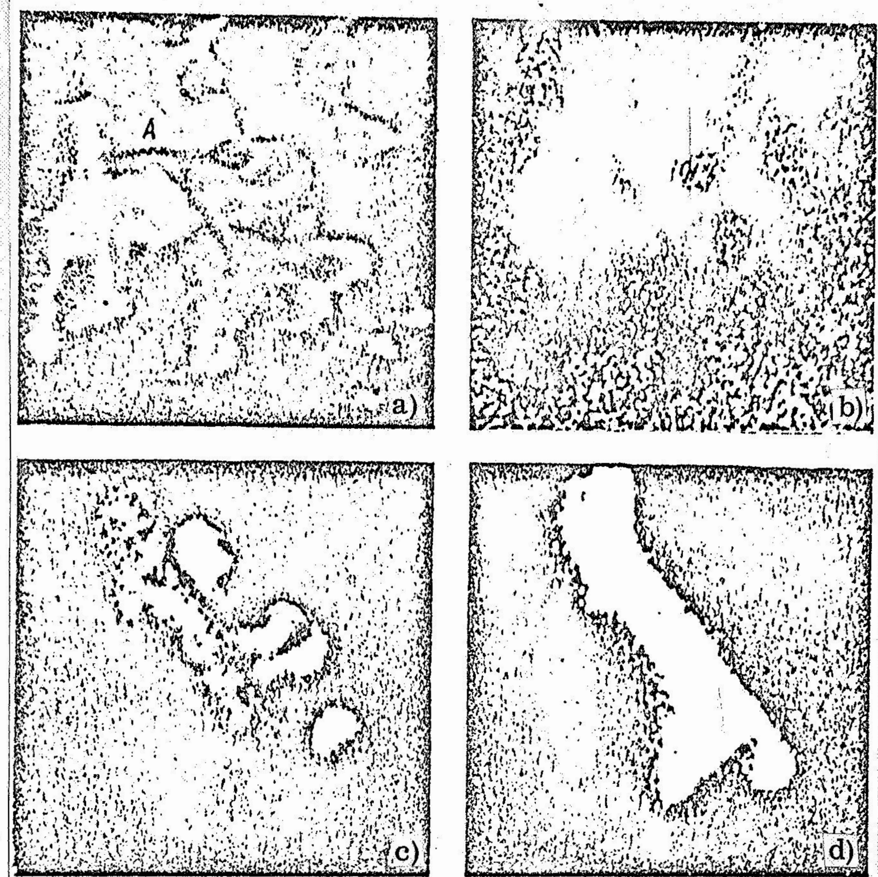

Figure 2. Distribution of the Elements in Cassiterite.

a) Picture in the Absorbed Electrons (Electron Absorption Coefficient Increases Inversely With the Mean Atomic Number. Light Fields Correspond to Concentration of the Lighter Elements; Dark Fields -- of the Heavier Elements; b) Picture in $Sn_{L\alpha}$ Radiation; c) Picture in $Fe_{K\alpha}$ Radiation; d) Picture in $Ti_{K\alpha}$ Radiation. Magnif. x 1,000.

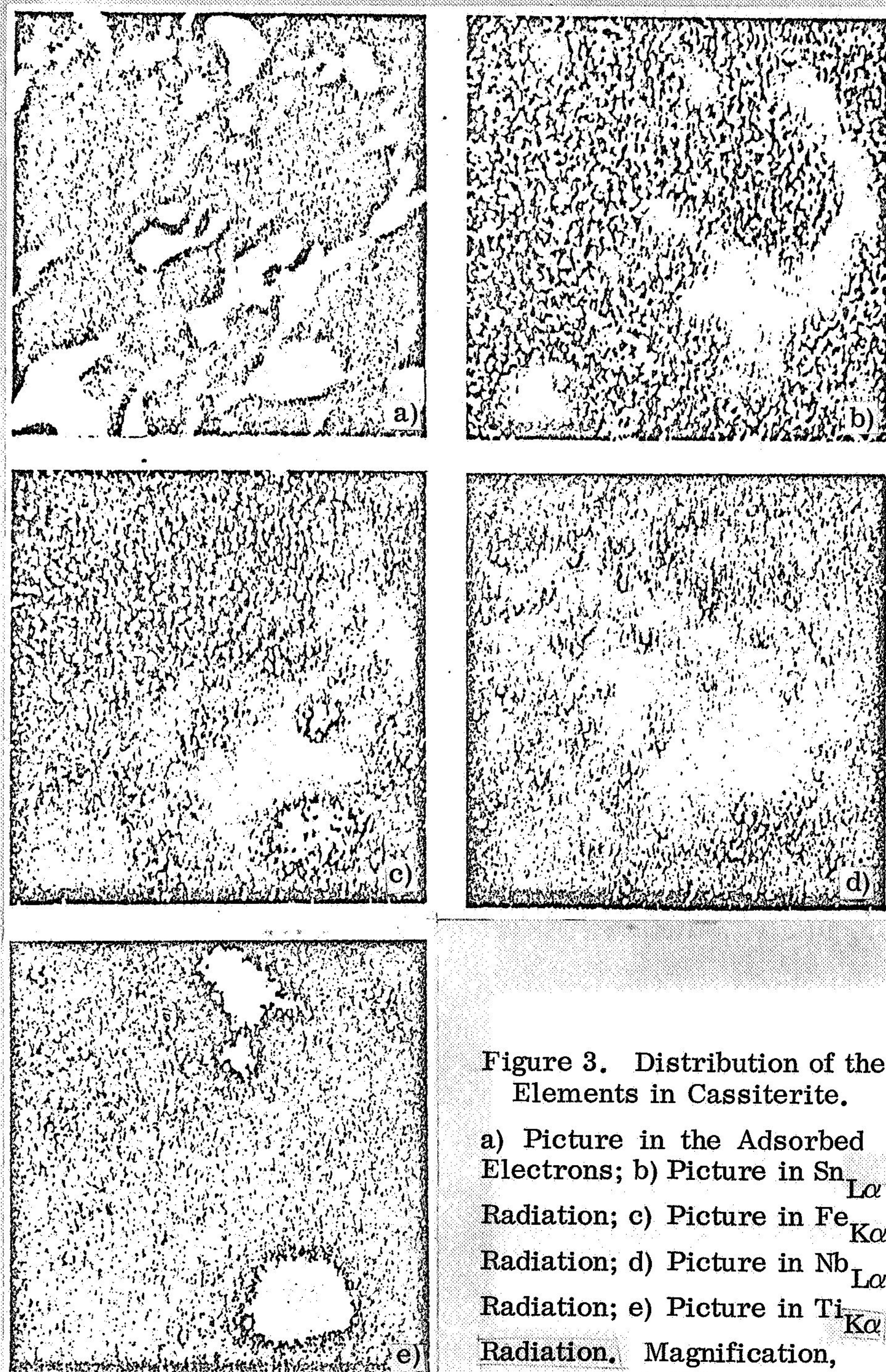

Figure 3. Distribution of the Elements in Cassiterite.

a) Picture in the Adsorbed Electrons; b) Picture in $Sn_{L\alpha}$ Radiation; c) Picture in $Fe_{K\alpha}$ Radiation; d) Picture in $Nb_{L\alpha}$ Radiation; e) Picture in $Ti_{K\alpha}$ Radiation. Magnification, x 1,000.

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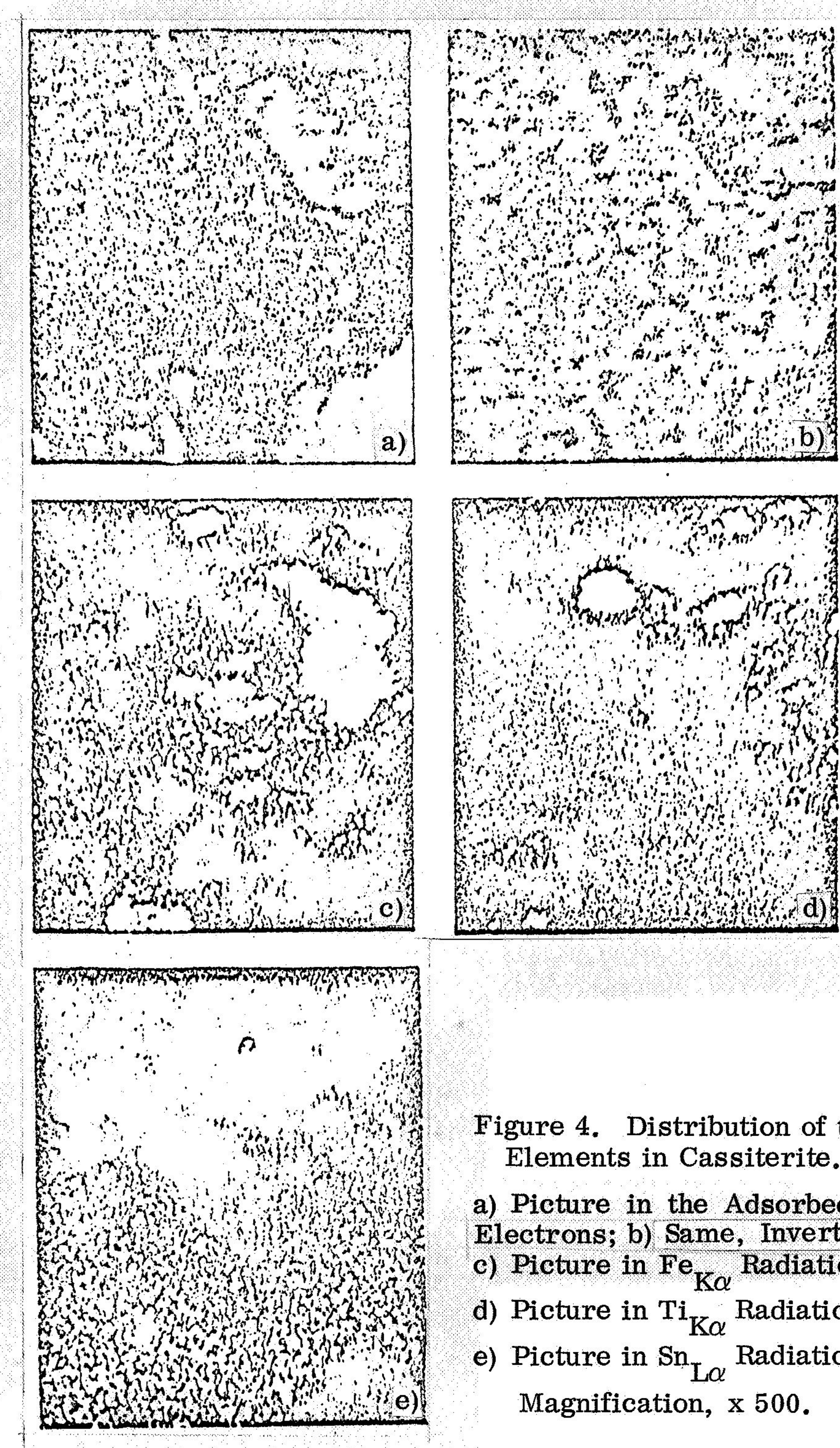

Figure 4. Distribution of the Elements in Cassiterite.

a) Picture in the Adsorbed Electrons; b) Same, Inverted; c) Picture in $Fe_{K\alpha}$ Radiation; d) Picture in $Ti_{K\alpha}$ Radiation; e) Picture in $Sn_{L\alpha}$ Radiation. Magnification, x 500.

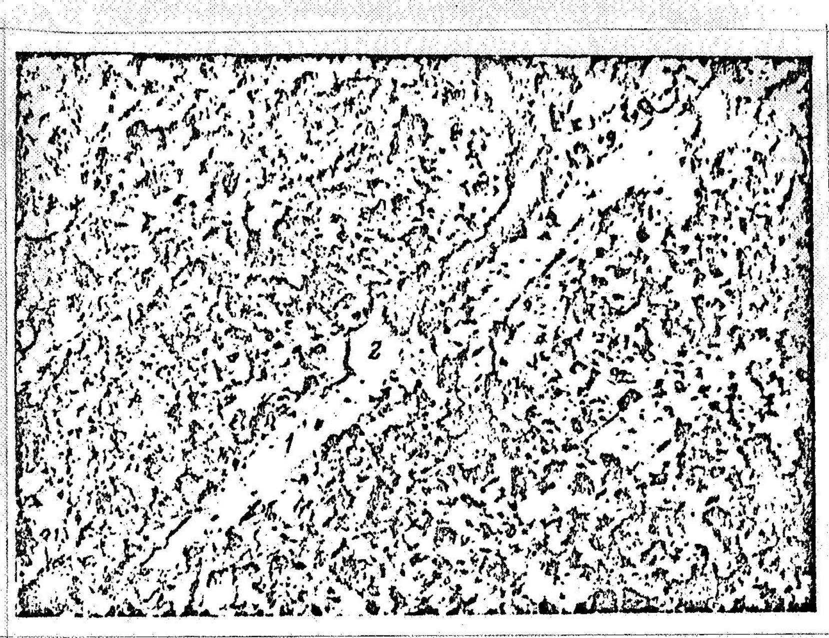

Figure 5. Tapiolite (1) and Wolframite (2) Growing Together in Cassiterite. Polished Section 12/Er. Etyka Ore Deposit. Magnification, x 450.

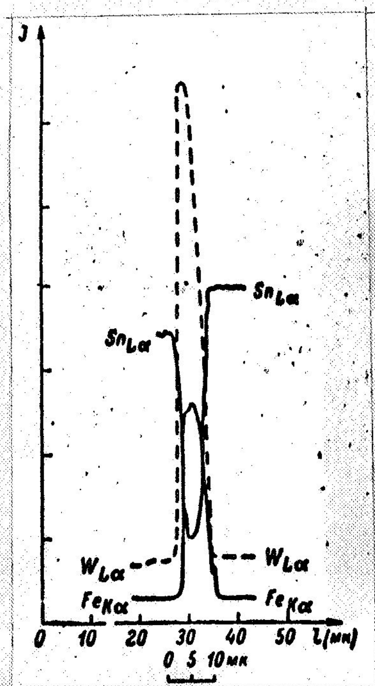

Figure 6. Changes in the Intensity of Characteristic Lines for Fe, W, and Sn, in Electron Ray Scanning Along a Wolframite Inclusion in Cassiterite From the Etyka Ore Deposit.

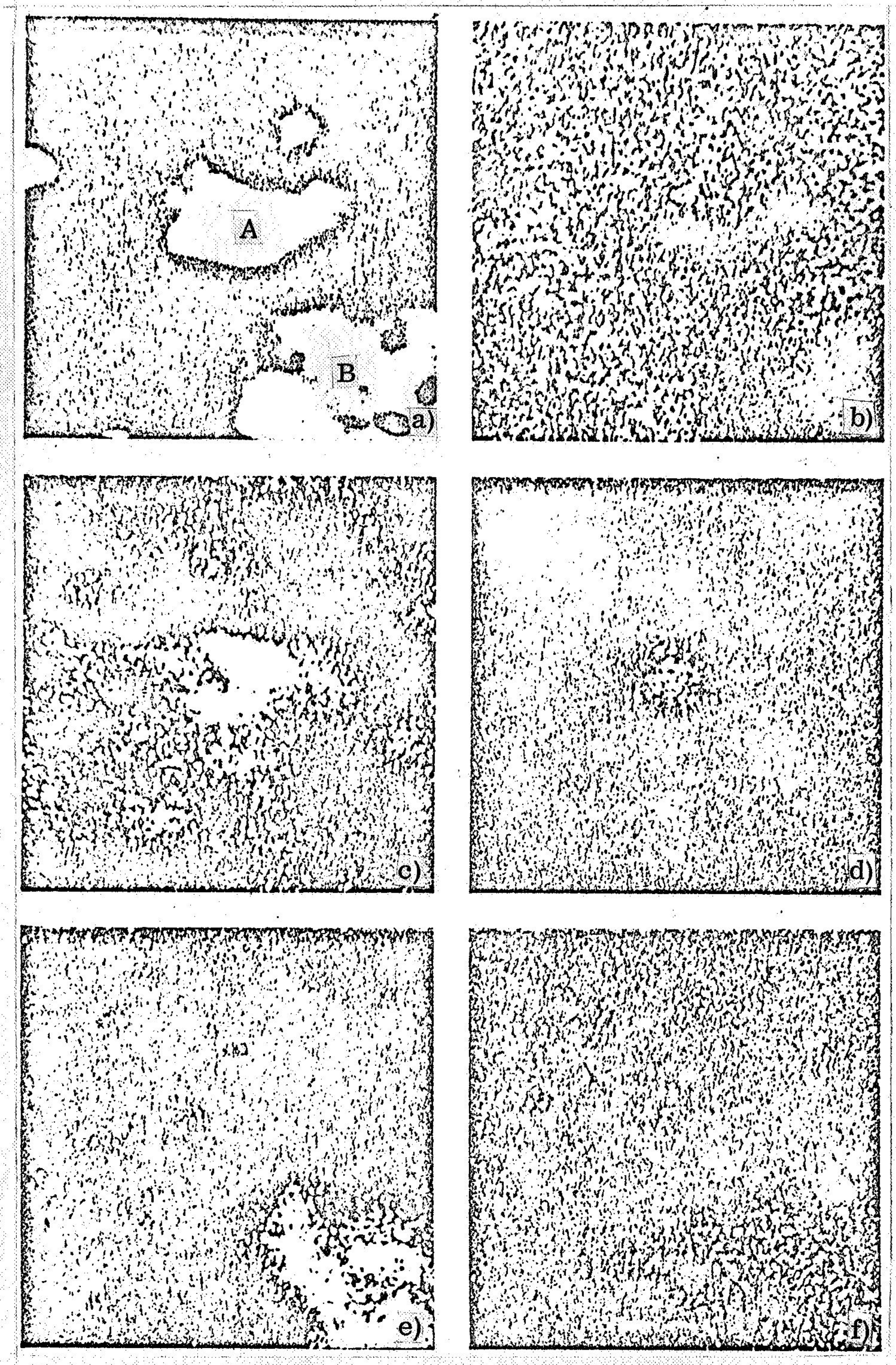

Figure 7. Distribution of the Elements in Cassiterite.

a) Picture in the Absorbed Electrons (A-Corundum Inclusion; B-Inclusion of a Mineral Containing Cu and Cl); b) Picture in $Sn_{L\alpha}$ Radiation; c) Picture in $Cr_{K\alpha}$ Radiation; d) Picture in $Al_{K\alpha}$ Radiation; e) Picture in $Cu_{K\alpha}$ Radiation; f) Picture in $Cl_{K\alpha}$ Radiation. Because of the Low Sensitivity of the Instrument to $Al_{K\alpha}$ and $Cl_{K\alpha}$ Radiations, Their Picture is not as Bright as That for $Cr_{K\alpha}$ and $Cu_{K\alpha}$. Magnif. x 1,000.

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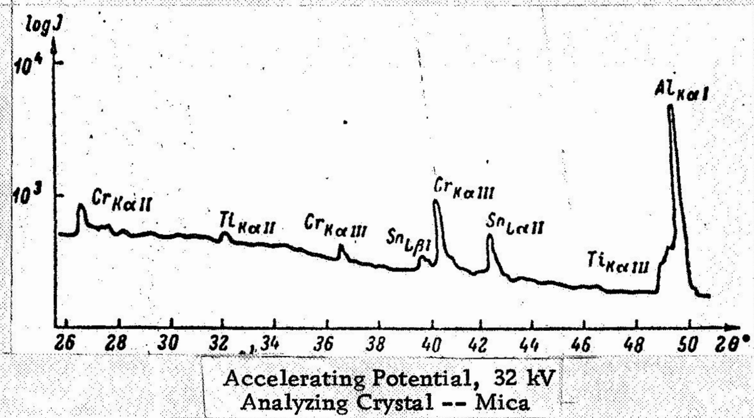

Figure 8. X-Ray Spectrogram of a Corundum Inclusion in Cassiterite From the Etyka Ore Deposit (see Fig. 7).

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